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## **A Novel Approach to Obtain GeSbTe-Based High Speed Crystallizing Materials for Phase Change Optical Recording**

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### **ABSTRACT**

A new approach is proposed to obtain fast crystallizing materials based on a conventional GeSbTe alloy for rewritable phase change optical data storage. By means of co-sputtering, Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> alloy was mixed with Sn<sub>1</sub>Bi<sub>2</sub>Te<sub>4</sub> alloy so as to form pseudo-binary alloys (Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub>)<sub>1-x</sub>(Sn<sub>1</sub>Bi<sub>2</sub>Te<sub>4</sub>)<sub>x</sub> (x is a mole fraction). From structural and optical analyses of the co-sputtered and annealed alloy films, the formation of stable crystalline single phases was observed along with a Vegard's law behavior, suggesting a homogeneous mixing of the two alloys. By use of a 4 layered disk with (Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub>)<sub>0.85</sub>(Sn<sub>1</sub>Bi<sub>2</sub>Te<sub>4</sub>)<sub>0.15</sub> recording layer, a preliminary test of writing and erasing was carried out and the results were compared with the case of the disk with Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> recording layer. The (Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub>)<sub>0.85</sub>(Sn<sub>1</sub>Bi<sub>2</sub>Te<sub>4</sub>)<sub>0.15</sub> recording layer was found to yield markedly higher erasability, especially with increasing disk linear velocity.

### **INTRODUCTION**

With a rapid progress of information and communication technology, there has been growing need for higher density and higher speed information storage. As for phase change optical data storage, boost in recording density and data transfer rate has been achieved primarily by ways of reduction in beam spot size and/or increase in disk linear velocity. Beam dwell time, expressible in terms of beam spot size divided by linear velocity, has diminished accordingly. This has led to a sustaining demand for faster crystallizing recording materials. In the cases of the GeSbTe alloys, enhanced crystallization kinetics has been attained by modification of alloy composition through addition of single elements such as Au, Pb[1,2], N[3], Sn[4], Bi[5] and/or by use of

crystallization promoting layers such as SiC, GeN[6,7]. In this report, we propose a novel approach that may be utilized to promote the crystallization kinetics of the GeSbTe alloys. In doing so, we address specifically the case of the stoichiometric  $\text{Ge}_1\text{Sb}_2\text{Te}_4$  alloy that is presently in wide use besides  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  alloy.

## PROPOSED APPROACH AND EXPERIMENTAL ALLOY SYSTEM

The present approach hinges on a well-known fact that a stoichiometric compound alloy tends to have faster kinetics of amorphous to crystalline transformation since only short range atomic reconfiguration would attend the transformation. An interesting question arises; suppose a stoichiometric alloy is mixed with another alloy that has the same stoichiometry but with a stronger tendency for crystallization, would the resulting alloy have an enhanced crystallization kinetics ?

Herein, we mix  $\text{Ge}_1\text{Sb}_2\text{Te}_4$  alloy with an isomorphous ternary alloy  $\text{Sn}_1\text{Bi}_2\text{Te}_4$  of the same stoichiometry.  $\text{Sn}_1\text{Bi}_2\text{Te}_4$  alloy is selected on the following bases. Firstly, Sn and Bi belong to the same family as Ge and Sb, but the bond energies of Sn-Sn, Bi-Bi, Sn-Te and Bi-Te are less than those of Ge-Ge, Sb-Sb, Ge-Te and Sb-Te, respectively[8]. We consider that the reduced bond energies would lead to the enhanced nucleation kinetics during amorphous to crystalline transformation of the mixed alloy. Secondly, the equilibrium crystalline phase of  $\text{Sn}_1\text{Bi}_2\text{Te}_4$  alloy has the same space group symmetry as that of  $\text{Ge}_1\text{Sb}_2\text{Te}_4$  alloy, with only a slight difference in lattice parameters ( $a=0.421$  nm,  $c=4.06$ nm for  $\text{Ge}_1\text{Sb}_2\text{Te}_4$  and  $a=0.441$  nm,  $c=4.1511$  nm for  $\text{Sn}_1\text{Bi}_2\text{Te}_4$ )[9,10]. These, together with similar melting temperatures of the two alloys[11]( $615^\circ\text{C}$  for  $\text{Ge}_1\text{Sb}_2\text{Te}_4$  and  $596^\circ\text{C}$  for  $\text{Sn}_1\text{Bi}_2\text{Te}_4$ ), suggest that the two alloys may have a strong tendency to form a homogeneous single phase solid solution over a wide range of mixing.

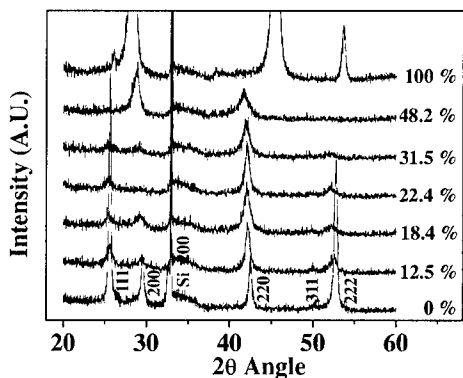
## EXPERIMENTS

Targets of  $\text{Ge}_1\text{Sb}_2\text{Te}_4$  and  $\text{Sn}_1\text{Bi}_2\text{Te}_4$  alloys were co-sputtered in a RF magnetron sputter system. In order to produce thin films of varying composition  $(\text{Ge}_1\text{Sb}_2\text{Te}_4)_{1-x}(\text{Sn}_1\text{Bi}_2\text{Te}_4)_x$ , sputtering power for a  $\text{Ge}_1\text{Sb}_2\text{Te}_4$  alloy target was varied with the power for  $\text{Sn}_1\text{Bi}_2\text{Te}_4$  target constant. From RBS (Rutherford Backscattering Spectrometry) spectra of the sputtered films, elemental compositions of Ge and Bi, yielding clearly separable RBS peaks from the rest, were determined and in turn overall compositions were estimated in terms of the mole fraction  $x$  assuming the respective stoichiometry of  $\text{Ge}_1\text{Sb}_2\text{Te}_4$  and  $\text{Sn}_1\text{Bi}_2\text{Te}_4$  is preserved during sputtering. For crystallization, co-sputtered films were annealed either at  $150^\circ\text{C}$  or at  $300^\circ\text{C}$  for 30 minute

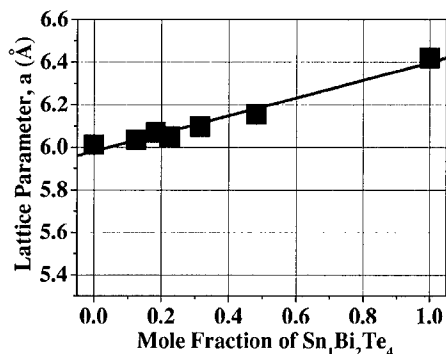
in a vacuum furnace with Ar flow. Structural analyses of films were made with XRD(X-ray Diffractometer, M18XHF-SRA). Refractive indices ( $n$ ) and extinction coefficients ( $k$ ) of films were determined from the simulation of phase difference( $\Delta$ ) and azimuth angle( $\Psi$ ) measured with variable angle spectroscopic ellipsometer (VASE) using the Lorentz-Drude oscillation model. Disk samples with recording layers of selected compositions were tested with a laboratory-built disk dynamic tester equipped with a laser diode of  $\lambda=650$  nm and an objective lens of N.A.=0.6.

## RESULTS AND DISCUSSIONS

Shown in figure 1 are the X-ray diffraction spectra of the co-sputtered films of various compositions ( $x = 0, 0.125, 0.1837, 0.2244, 0.3152, 0.4818, 1$ ) annealed at  $150^\circ\text{C}$ . It is found that diffraction spectra for each composition can be indexed as a crystalline FCC single phase except for the  $\text{Sn}_1\text{Bi}_2\text{Te}_4$  case ( $x=1$ ). A sputtered film of the  $\text{Sn}_1\text{Bi}_2\text{Te}_4$  alloy was found to exist as an FCC phase in the as-deposited state and as a two phase mixture of an FCC and an HCP in the annealed state. From figure 1, one should notice a telling feature with increasing mole fraction  $x$ . Each peak, for instance 220 peak, undergoes a positional shift toward a smaller  $2\theta$  angle with a concomitant gradual peak broadening. Without homogeneous mixing of  $\text{Sn}_1\text{Bi}_2\text{Te}_4$  and  $\text{Ge}_1\text{Sb}_2\text{Te}_4$  on an atomic scale, each FCC peak would appear two split peaks with relative intensity ratio continuously changing with mole fraction  $x$ . Quite possibly, the peak broadening is then considered to result from lattice distortion due to accommodation of atoms



**Figure 1.** X-Ray diffraction spectra of the co-sputtered  $(\text{Ge}_1\text{Sb}_2\text{Te}_4)_{1-x}(\text{Sn}_1\text{Bi}_2\text{Te}_4)_x$  films annealed at  $150^\circ\text{C}$ . Peaks can be indexed as an



**Figure 2.** Variation of lattice parameter with the mole fraction ( $x$ ) of  $\text{Sn}_1\text{Bi}_2\text{Te}_4$ , as measured from co-sputtered  $(\text{Ge}_1\text{Sb}_2\text{Te}_4)_{1-x}(\text{Sn}_1\text{Bi}_2\text{Te}_4)_x$  films annealed at  $150^\circ\text{C}$ .

with different sizes. The dependence of FCC lattice parameter on the mole fraction  $x$ , as suggested by the shift of the peak position, was determined from diffraction spectra as shown in figure 2. One can clearly see a nearly linear relationship representing a Vegard's law behavior as expected for a homogeneous solid solution. A similar relationship were also observed from the co-sputtered films annealed at 300 °C where an HCP phase is the prevailing crystalline state for the entire range of mole fraction.

Optical constants of the as-deposited films as well as the annealed films have been determined, from which optical band gap energies were derived. The results are summarized in figure 3, depicting the dependence of optical band gap energy on  $\text{Sn}_1\text{Bi}_2\text{Te}_4$  content in the co-sputtered alloys of various structural states. As for both annealed films, optical band gap energy has a very weak compositional dependence with increasing  $\text{Sn}_1\text{Bi}_2\text{Te}_4$  content. As for as-deposited films, the trend runs similar up to around  $x=0.15$  where band gap energy undergoes a steep decrease in conjunction with the appearance of the crystalline as-deposited state.

In order to find out whether the present approach can be applied to high speed phase change optical storage, dynamic tests of the disks were carried out using disk samples of 4 layer stacks consisting of  $\text{AlCr}(100 \text{ nm}) / \text{ZnS-SiO}_2(20 \text{ nm}) / \text{Active layer}(20 \text{ nm}) / \text{ZnS-SiO}_2(270 \text{ nm})$  on 1.2 mm polycarbonate substrate. As for active layers,  $(\text{Ge}_1\text{Sb}_2\text{Te}_4)_{0.85}(\text{Sn}_1\text{Bi}_2\text{Te}_4)_{0.15}$  alloy was selected along with  $\text{Ge}_1\text{Sb}_2\text{Te}_4$  alloy for comparison (for brevity, a disk with the  $(\text{Ge}_1\text{Sb}_2\text{Te}_4)_{0.85}(\text{Sn}_1\text{Bi}_2\text{Te}_4)_{0.15}$  recording layer is denoted hereafter as disk A and the one with the  $\text{Ge}_1\text{Sb}_2\text{Te}_4$  as disk B). Reflectivity values of the as-deposited amorphous ( $R_a$ ) and initialized crystalline ( $R_x$ ) states, as measured with  $\lambda=650 \text{ nm}$  and  $\text{N.A.}=0.6$  optics of the disk tester, were respectively 3 % and 11 % for disk A and 3.5 % and 10 % for disk B.

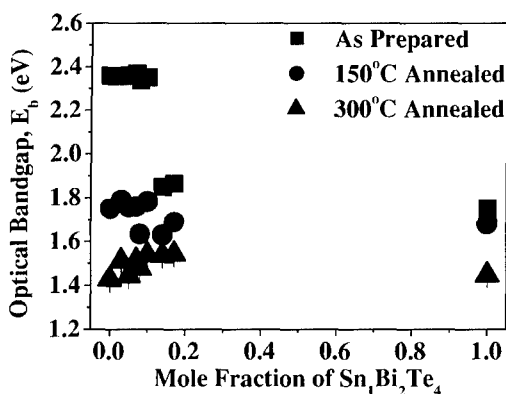


Fig 3. Dependence of optical band gap energy on the mole fraction of  $\text{Sn}_1\text{Bi}_2\text{Te}_4$ , as measured from co-sputtered  $(\text{Ge}_1\text{Sb}_2\text{Te}_4)_{1-x}(\text{Sn}_1\text{Bi}_2\text{Te}_4)_x$  films of various structural states.

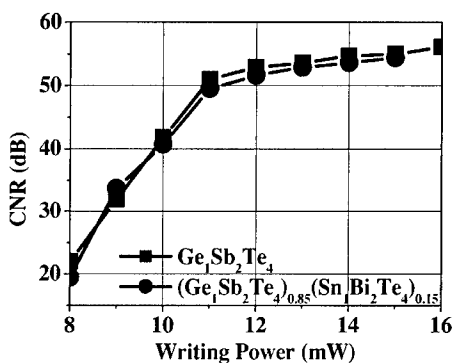


Fig 4. Comparison of writing power dependence of CNR between disks of the two different recording layer materials

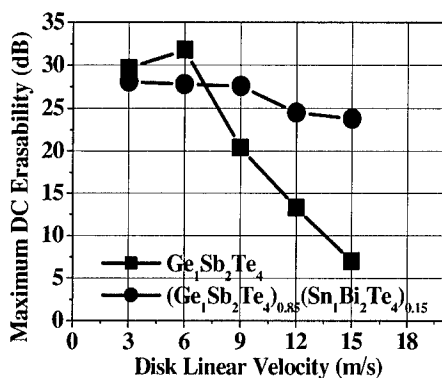


Fig 5. Comparison of the dependence of maximum DC erasability on the disk linear velocity, between disks of the two different recording layer materials

Writing of amorphous marks was performed at the linear velocity of 9 m/s by use of a writing pulse consisting of a writing power level of  $3T_w$  ( $T_w=23.3$  nsec) duration followed by a readout power level (1 mW) of  $7T_w$  duration. In figure 4, CNR values are shown as a function of writing power, measured at the readout frequency of 4.29 MHz. Between the two disks, CNR values appear remarkably similar with only 1 to 2 dB difference regardless of a writing power. Since contrast ratio  $(R_x - R_a)/(R_x + R_a)$  difference between the two disks (0.48 for disk A and 0.57 for disk B) accounts for 1.5 dB CNR difference, it follows that sizes of amorphous marks may be comparable between the two disks and thermal constants of the recording layers as well.

In contrast to writing, a striking difference was observed between the two disks during erasing. For this experiment, amorphous marks were formed with 15mW writing power under the same writing conditions specified above and subsequently DC-erased while varying disk linear velocity. In figure 5, maximum DC erasability due to a respective optimum erasing power is shown as a function of linear velocity. As for disk A, erasability decreases very rapidly with disk linear velocity, reaching below 20 dB near 9 m/s. On the contrary, disk B displays no appreciable decrease with increasing disk linear velocity but maintains a high erasability around 25 dB even at the velocity of 15 m/s.

## CONCLUSION

An approach is proposed to obtain fast crystallizing materials for rewritable phase change optical storage. The approach makes a purposeful use of a homogeneous mixing of a conventional stoichiometric GeSbTe alloy with an isomorphous alloy of the same stoichiometry but with a stronger tendency for crystallization. By means of co-sputtering,  $\text{Ge}_1\text{Sb}_2\text{Te}_4$  alloy was mixed with  $\text{Sn}_1\text{Bi}_2\text{Te}_4$  alloy and preliminary analyses of the co-sputtered films were carried out. Evidences of a homogeneous mixing as well as of a promoted crystallization were attained. We suppose that faster crystallization of the co-sputtered alloys may result from the reduced pairwise bond energies particularly of Sn-Te and Bi-Te relative to Ge-Te and Sb-Te by way of promotion of nucleation kinetics.

## ACKNOWLEDGMENT

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